



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> :

C01F 11/18

A1

(11) International Publication Number:

WO 97/38940

(43) International Publication Date:

23 October 1997 (23.10.97)

(21) International Application Number: PCT/FI97/00238

(22) International Filing Date: 17 April 1997 (17.04.97)

(30) Priority Data:

961675

17 April 1996 (17.04.96)

FI

964129

14 October 1996 (14.10.96)

FI

(71) Applicant (for all designated States except US): KAUTAR OY  
[FI/FI]; T-linja 38 A, FIN-37800 Toijala (FI).

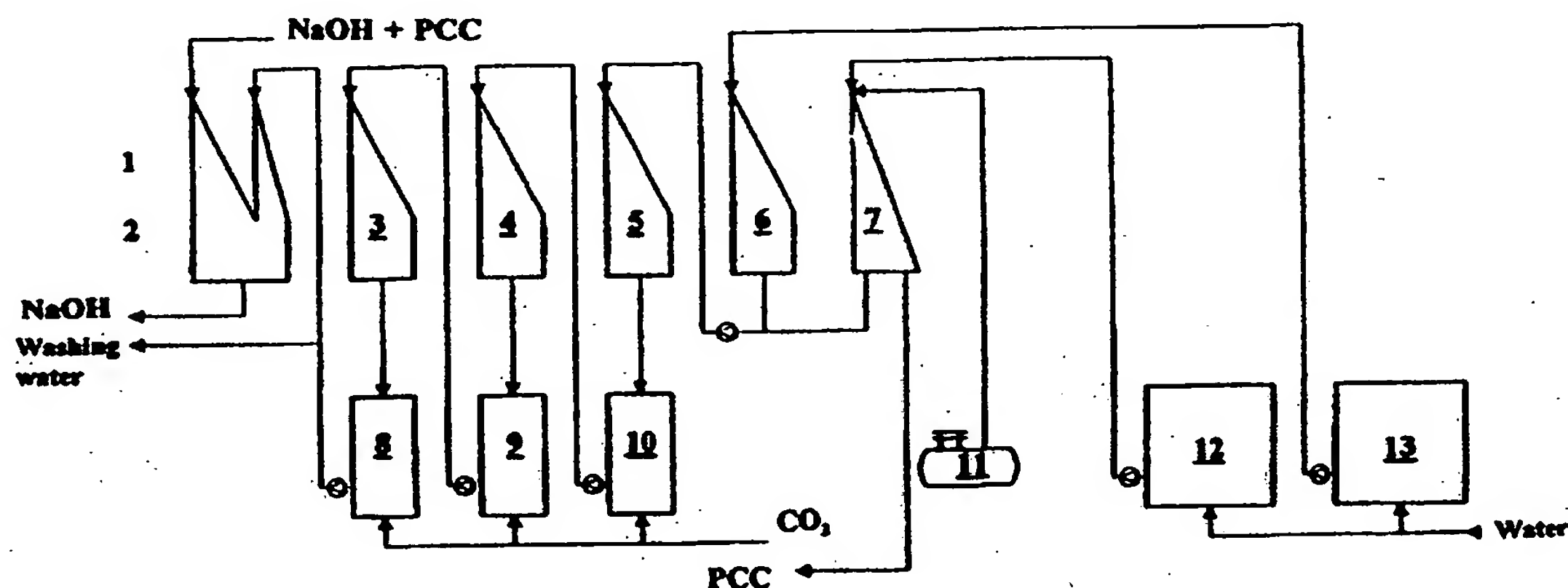
(72) Inventor; and

(75) Inventor/Applicant (for US only): VIRTANEN, Pentti [FI/FI];  
T-linja 38 A, FIN-37800 Toijala (FI).(74) Agents: LAINE, Seppo et al.; Seppo Laine Oy, Lönnrotinkatu  
19 A, FIN-00120 Helsinki (FI).(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR,  
BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE,  
HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT,  
LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT,  
RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG,  
US, UZ, VN, YU, ARIPO patent (GH, KE, LS, MW, SD,  
SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU,  
TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI,  
FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent  
(BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD,  
TG).

Published

With international search report.

In English translation (filed in Finnish).

(54) Title: METHOD AND APPARATUS FOR RECOVERING  $\text{CaCO}_3$  PRODUCED BY CAUSTICIZING

## (57) Abstract

The invention relates to a method and apparatus for recovering precipitated calcium carbonate, PCC, prepared by a causticizing reaction. According to the method PCC is separated from the reaction mixture of the causticizing reaction by filtration, and the PCC-containing precipitate collected onto a filter (3-5) is washed with water, in order to separate by-products from the PCC. According to the invention the PCC precipitate is washed with water into which carbon dioxide is dissolved to a sufficient extent to convert at least part of the hydroxy compounds in the precipitate into the corresponding carbonate compounds. Most suitably carbon dioxide is used in an amount that is at the most 20 % in excess in comparison to the hydroxy compounds. The apparatus of the invention comprises several pressure filtration units (3-5), with which calcium carbonate may be separated from the reaction mixture, and each of which has its own input line for adding the liquid to be filtered, the wash liquid for calcium carbonate and the neutralizing liquid for calcium carbonate into the filtration unit.

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## **Method and apparatus for recovering $\text{CaCO}_3$ produced by causticizing**

The present invention relates to a method according to the preamble of Claim 1 for recovering precipitated calcium carbonate (PCC).

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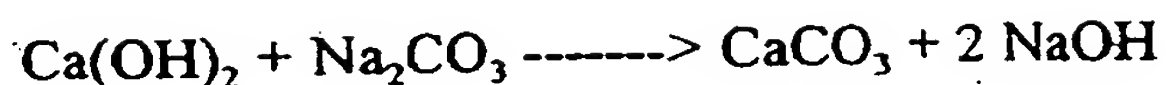
According to the method of this invention PCC is first separated from the reaction mixture of the causticizing reaction by filtration, and the PCC-containing precipitate collected on the filter, or the filtration cake, is washed with water in order to separate by-products and impurities from the PCC product. This invention also relates to the (secondary)

10 neutralization and dispersion of calcium carbonate treated according to the manner described above.

This invention also relates to an apparatus as set forth in the preamble of Claim 18 for recovering calcium carbonate from reaction media containing hydroxy compounds. An  
15 apparatus of this type usually comprises at least one pressure filtration unit for separating calcium carbonate from the reaction medium, and a tank for wash liquid that is connected to the pressure filtration unit, from which wash liquid can be fed into the filtration unit for washing the calcium carbonate.

20 Synthetic or in other words industrial or precipitated calcium carbonate, which is referred to in the following as PCC (Precipitated Calcium Carbonate), has become more and more widely used as a filler or mixed pigment in the chemical, pharmaceutical, plastics and paper industries and as a coating pigment for paper.

25 The calcium carbonate used in the paper industry is generally produced by carbonating calcium hydroxide with carbon dioxide obtained from the exhaust gases of combustion processes. The precipitated calcium carbonate can also be prepared by a process known as causticizing, in which a calcium oxide-based starting material, which contains hydrated calcium oxide (or calcium hydroxide), is reacted with carbonate ions in an aqueous medium  
30 to obtain an aqueous suspension containing calcium carbonate. The reaction takes place according to the following equation:



The specific problems in the causticizing process have been the dilute concentration of the lye produced, achieving the separation of the precipitated PCC crystals from the lye solution in an economical way, and the agglomeration of the crystals obtained. Some uncausticized carbonate always remains in the lye solution, and a portion of the calcium remains in the form of a hydroxide. Accordingly, the product of the causticizing reaction, calcium carbonate, contains lye and calcium hydroxide as by-products and impurities, which renders it necessary to wash the PCC carefully with water and to neutralize it before a useful product can be obtained. As far as the concentration of the lye solution is concerned, it must be stated that in the first stage of the reaction it is necessary that the reaction medium is dilute enough with respect to the reactants, in order to ensure that the equilibrium of the causticizing reaction is on the right-hand side. When the concentration of the carbonate and the corresponding concentration of lye are dilute, the reaction will take place nearly completely, although it will never reach completion entirely.

It is an object of the present invention to remove the disadvantages of the techniques according to the known art and to provide a novel solution, which is economical and which comprises advantageous process conditions, for the recovery of calcium carbonate of desired dry substance content from the reaction mixture of the preparative reaction.

It is a further object of the invention is to provide a novel method for the washing and drying of the precipitated material.

The invention is based on washing and pre-neutralizing calcium carbonate separated from the reaction mixture with water which contains carbon dioxide dissolved in the water in an amount sufficient to enable the conversion of at least a proportion of the hydroxy compounds in the precipitate to the corresponding carbonate compounds. Therefore, the wash liquid tank of the apparatus has been equipped with an input line for carbon dioxide, through which carbon dioxide may be added to the wash liquid.

By dissolving CO<sub>2</sub> into the water intended for washing, it is possible to convert the sodium hydroxide and the calcium hydroxide mixed with the PCC from the causticizing reaction, or the calcium hydroxide mixed with the PCC obtained by a carbonation reaction, respectively, into the corresponding carbonate compounds according to the following reaction equations:

1.  $2 \text{ NaOH} + \text{CO}_2 \longrightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$
2.  $\text{NaOH} + \text{CO}_2 \longrightarrow \text{NaHCO}_3$
3.  $\text{Ca(OH)}_2 + \text{CO}_2 \longrightarrow \text{CaCO}_3 + \text{H}_2\text{O}$

Most suitably CO<sub>2</sub> is used in an equivalent amount compared to the hydroxy compounds, or possibly slightly in excess (+10 ... +20 %).

According to an especially preferred embodiment the carbon dioxide dissolved into the wash liquid is released in the filtration zone, which causes the gas bubbles to effect foam formation in the filtrate cake, to dry it and to prevent the formation of channels in the cake at the same time. The gas may be released by reducing pressure and/or by heating.

More specifically, the method of the present invention is mainly characterized by what is stated in the characterizing part of Claim 1.

The apparatus of the present invention is characterized by what is stated in the characterizing part of Claim 18.

In the following, the present invention will be described in more detail by using the treatment of the product obtained in a causticizing reaction as an example. Nevertheless, it is to be understood that washing in accordance with the invention and in particular drying according to a preferable embodiment are equally suitable for the treatment of a product prepared by carbonation.

The method of the invention comprises the following steps, the last two of which are optional but advantageous:



- separation of PCC from a sodium hydroxide solution by precipitation,
- washing PCC with carbon dioxide-containing water,
- final neutralization of PCC with a mineral acid, and
- dispersion of PCC and adjustment of solids content.

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According to a preferable embodiment of the invention the separation of PCC from the NaOH solution, the washing of PCC, the neutralization of residual NaOH and  $\text{Ca}(\text{OH})_2$  with  $\text{CO}_2$ , the final neutralization with  $\text{H}_3\text{PO}_4$ , and the addition of dispersion agent are performed in the filter. It is especially preferable to separate PCC from the NaOH solution, to wash and preneutralize it, to perform the final neutralization with acid and to add the dispersion agent in a filter with an operational ratio for different functions of greater than 50 %. The filter used is a pressure filter in which filtration is performed at a pressure of 2 - 20 bar. The different stages of the process are performed as a continuous stream, which minimizes variations in the input pressure and prevents crack formation in the filtrated cake.

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It is essential that in between the different stages of washing an excess pressure is maintained in order to prevent the filtrate cake from cracking. Simultaneously the solids content of the filtrate cake is kept constant. Most suitably the pressure is allowed to be reduced to 90 % at the most, preferably only to about 80 % of the pressure during the wash.

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Separation of PCC and NaOH, and washing of PCC and the different stages of treating it, take up operational time of the pressure filter to a considerable extent. In conventional pressure filters the filter part, a disk unit, is operational almost all the time, whereas the other parts of the apparatus, such as means for sealing, transferring, washing and discharging, are operational for only about 10 % of the operational time of the filter. Because the said means constitute almost 90 % of the cost of the filter, the process of the invention is rendered economically unprofitable in normal pressure and air filters. Conversion of the pressure filter into a processing apparatus is technically and economically a very profitable alternative. Therefore, the filter-processing apparatus of the invention enables one to perform time-consuming processes in the pressure filter. The filter-processing apparatus is economical mainly due to the fact that all principal parts of the filter-processing means operate at almost 100 % load.

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In brief, it can be said that the invention speeds up the recovery of calcium carbonate and reduces the capital expenditure on the filtration apparatus considerably.

The invention is described in the following in more detail with the aid of the enclosed figures, in which

Figure 1 is a schematic process drawing illustrating the principles of the method according to this invention, and

Figure 2 is a perspective drawing of the structure of the apparatus used according to the invention.

The stages of the method according to the invention are presented in Figure 1. It should be noted that in the figure all processes have been presented as separate items on the flow chart for the sake of simplicity, which does not preclude the possibility that all stages of the process from separation to neutralization may be performed in the same apparatus, namely the filter. In the following this preferable embodiment of this invention is described in more detail. However, the invention may be carried out in such a way that a separate unit is arranged for each step of the process when desirable.

#### A. Separation of NaOH

Calcium carbonate-containing suspension from the causticizing process is used as input for filtration 1, during which a reaction medium essentially comprising an aqueous solution of sodium hydroxide is separated from the calcium carbonate precipitate. According to the invention a pressure filter is used. A particularly preferable pressure filter type is the so called chamber filter, in which the filtering chambers are arranged horizontally. The retaining layer comprise a fabric, a filter membrane, a meshwork or a similar filtering layer.

The objective of the filtration is to achieve a ~ 40 % solids content. In connection with the filtration, a preliminary prewash 2 may be performed with water by using, for example, 1000 l H<sub>2</sub>O/1000 g PCC. The water used for washing is allowed to combine with the NaOH.

## B. The washing of PCC

The actual washing of PCC is performed, for example, as a 3-stage wash (reference numerals 3 - 5). This means that after each wash step the water used for washing is removed. As can be seen in Figure 1, the washing water is introduced into each washing step through one or more wash tanks (8 - 10). Carbon dioxide gas or carbon dioxide containing gas is dissolved into the washing water at least in an amount that is sufficient to neutralize the residual lye according to the reaction equation  $2 \text{NaOH} + \text{CO}_2 \rightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O}$ . Preferably a 5 - 20 %, and typically about a 10 % excess of carbon dioxide is used.

The gas may be dissolved into the washing solution at normal pressure or preferably at elevated pressure or excess pressure. Usually the excess pressure is 1.01 - 50 bar, preferably about 2 - 20 bar.

The washing water is recycled and used for the  $\text{Na}_2\text{CO}_3$  solution of the causticizing process.

Washing is most suitably performed in such a manner that the PCC particles are in liquid phase. Intermediate drying with air is not necessary. Washing is preferably performed under pressure in such a way that between different steps of washing pressure is not reduced by more than 50 %. Typically filtration is performed at a pressure of 2 - 20 bar, preferably at 3 - 15 bar. The tanks for the wash solution are kept at a corresponding pressure. Also carbon dioxide is input at a similar pressure into the tanks for the wash solution. After washing, the solids content of the filtered PCC cake is approximately 40 %.

The carbon dioxide gas used may comprise pure gas. Alternatively the carbon dioxide may originate from exhaust gases in smoke or from the exhaust of a lime kiln.

As has already been described above, according to one preferable embodiment the gas dissolved into the wash solution of the filter cake, or carbon dioxide in this case, is released inside the filter cake to dry this. This embodiment may be performed, for example, in the



following manner: filtration zone or filtration chamber is filled with liquid containing dissolved gas, which replaces the input solution remaining in between the filtered particles. After this pressure is slowly reduced, starting from the filtrate zone or the filtrate side of the filter, which causes the gas bubbles to become released and grow in larger size according to the extent of pressure reduction. The gas bubbles begin to form on the surfaces of small filtered particles, and "foam" the otherwise tightly packed filter cake in a homogeneous manner, and prevent this from shrinking and cracking. According to the method described above neither cracking nor the formation of a uniform network of channels takes place. The formation of bubbles causes the resistance to flow in the filter cake to be reduced, and washing and simultaneous blow drying of the cake can be achieved with a smaller pressure difference than usually.

According to this invention drying takes place with the same released gas, which forces the wash solution out of the filtered cake.

The filtered cake may be warmed during drying, for example, by directing hot vapor or gas into the filtering chamber. The vapor used may comprise steam at normal or excess pressure, or heated gas (for example, air). Heating facilitates both drying and the release of gas from the wash solution.

### C. Neutralization of PCC

As has been described above, the neutralization of PCC is essentially performed in connection with the washing step. The exact pH value for neutralization can be achieved when desirable by washing the filtered cake with an aqueous solution that contains mineral acid, for example,  $H_3PO_4$ . Neutralization is referred to by the reference numeral 6.

During neutralization pressure is maintained within the same limits as during washing, that is, at 2 - 20 bar, and the solids content of the PCC cake at approximately 40 %. The aqueous filtrate obtained is used as washing water for the preceding washing steps.

#### D. Dispersion

During the dispersion step the filtered, washed and neutralized PCC precipitate is resuspended by adding a dispersion agent which makes it fluid again. The suspension  
5 obtained may be used as such, but its solids content may be increased to 50 - 80 % as is described in the following.

Because the PCC precipitate contains very small particles, the van der Waals forces between the crystals are quite strong, and it is not possible to manipulate the particles  
10 without the aid of a dispersing agent. Commonly known polyelectrolytes, like polyacrylate, may be used as the dispersing agent or disperser.

The dispersion step is most suitably carried out in two stages, whereby most of the dispersing agent is added to the filtered cake in the filter, whereafter the rest is added while  
15 the filtered cake is suspended. This enables adjusting the viscosity of the PCC suspension accurately to the desired value. Typically the desirable value for viscosity is, for example, 100 - 500 cP, preferably about 200 - 400 cP. The addition of dispersing agent in the filter is most suitably carried out such that about 60 % of the dispersing agent is added to the PCC  
20 cake in the filter. The pressure variation is the same as is used for washing, and the solids content of PCC is about 40 %. The aqueous filtrate is used for washing. The rest of the dispersing agent, that is, about 40 %, is only added to the mixer when the PCC cake is being resuspended. The material is dispersed rapidly as it already contains some dispersing agent. However, it is not advisable to add to the filter all of the dispersing agent, because  
25 this complicates separation of the filtered cakes from the filter disks.

The mixer used may be of the shock mixer type described below.

A solids content of approximately 50 % is achieved when pressurized air is blown through the PCC cake after dispersion, the pressure of the air being about 5 - 50 bar, typically about  
30 20 - 30 bar. However, it is not economically advantageous to dry the PCC product to greater than 50 % solids content with pressurized air. Such solids contents are achieved when, during the suspension of the PCC, an amount of the dispersing agent that almost

corresponds to the desired solids content, is added and the suspension is pressure filtered again. This makes it readily possible to achieve an approximately 60 % solids content, and even a 80 % solids content is achievable. It is preferred to use compression with the aid of a membrane in connection with blowing with pressurized air in the filter to increase the solids content. The filtrate that contains dispersing agent is used for predispersing in the pressure filter.

The principles of the structure of the pressure filtration system used according to the invention are described in Figure 2. The fundamental principle of the apparatus according to the invention is that the various parts of the filtering system are used as efficiently as possible, that is, the degree of their operation should be as close to 100 % as possible. Therefore, the total filtering capacity of the filtration system of the invention has been distributed to several filtration units 21. In the embodiment according to Figure 2 there are eight of these units, but usually there are about 4 - 10 units. Each of these comprises a stack of disk filters of, for example, 10 - 30, typically about 20, filter disks. The filtration units are used in parallel such that simultaneously at least one filtration unit is used for the separation and prewashing of calcium carbonate, one or more (in 3-stage wash, for example, three) for washing the filtered cake, and at least one for further neutralization. In this case, the input lines 34 arranged into the apparatus for the mixture to be filtered, washing water and neutralizing solution, are also used simultaneously. Similarly, the collection means 30 and the discharging means 27 of the filter stacks of the filtration system are used continuously. This arrangement reduces the capital expenditure of the apparatus considerably.

The filtration disk stack comprises lid or end plates which may be equipped with a compressible rubber disk which can be used to buffer the pressure of the filtration unit between various process steps. This facilitates the prevention of crack formation in the cakes. Moreover, there is an input connection for the mixture to be filtered, the wash solution, the neutralizing solution and the dispersing agent, into the center of the end of a filtration disk stack. This makes it possible to add the mixture or the liquid, respectively, from the center of the stack, which causes the transfer distance for the liquid to be small, and addition and washing will take place in a homogeneous manner.

According to the embodiment illustrated in Figure 2 the filtration system is equipped with a compression means 22 for the filter disks, which causes the stacks to be compressed, in order to prevent them from breaking under the filtration pressure. Number 23 indicates a combined means for transferring and tightening the pressurized stacks, and 24 refers to a filtration stack that has already been processed, and has been removed from the row of filtering units with the aid of the transfer means 23. The transfer means 23 may be moved into position next to a desired stack with the aid of transferring means 23'. The processed stack 24 is moved to stack unpacking 27, for example, along rollers 25. At the end of the conveyor line hoisting means 27 are arranged which lift the stack to unpacking means 27. The hoisting means most suitably also comprise a balance for checking that the weights of the filtered cakes conform to default values. If variation occurs, this may indicate that one of the filter disks has been damaged. The filter disk stack is unpacked with the means 27 in which each filter disk is turned and emptied into the receiving funnel 28 for the filtered cakes. The used filter disks are transferred through wash 29 to the compiling means 30 of the filtration stacks where the stacks are reassembled. Each complete stack is in turn transferred along conveyor line 31 to the transferring and tightening means 23, at which the stacks are moved into a free position in the row of filtering units, and tightened according to the sealing pressure.

The cakes are transported from the receiving funnel 28 for the filtered cakes to a suspending means 33 with the aid of a conveyor belt 32. For example, a shock mixer may be used for this purpose. The term shock mixer used herein refers to an apparatus in which there are disk-like collision surfaces along rotating circumferences, the excessively large cutting force of which causes (after the collision) the liquid and the suspension to drain in the direction of the centrifugal force from the blades of the inner mixing disk to mixing blades of a concentric outer disk, which causes the mixture to be subjected to great cutting forces when it transfers from one blade to another, which forces are caused by the differences in the rotational speed and/or direction of successive blades. The apparatus is essentially used here such that liquid and suspension are input to it with a lower capacity of volume flow than that applied when they are removed. In such an apparatus the disks are arranged either radially or they are slightly tilted to the direction of rotation. The possibility of performing homogeneous mixing and to effect homogeneous cutting forces as a result of

collisions between solids and a solid collision surface in a shock mixer results in a more homogeneous result than in other types of mixers, when expressed as probabilities. Typically more than 95 % of the material flow receives almost 100 % of the maximal shock energy, and only 5 - 10 % of the material receives less than 60 % of the maximal shock energy. This distribution corresponding to the intensity of the turbulence of mixing is many times larger in other, even in the so-called "high shear" mixers of dissolver-type.

The filtering units are connected to input lines 34 at the top, which enables the addition of the suspension to be filtered as well as washing, neutralizing and dispersing agents. The reference numerals 35 - 37 refer to tanks for the washing, neutralizing and dispersing agents, respectively. The washing agent tanks 35 are equipped with input lines for carbon dioxide, which has been shown in Figure 1.

It is known that filter fabrics or membranes for small particles do not sustain great mechanical strain, wherefore they cannot be used in automatic filters in which the fabric is run as a belt over rollers which cause the fabric to be emptied of the filtered cake. In the filtration-processing apparatus according to the invention the filter fabric has not been given such integrated functions; its task is merely to function as the filtration means in the separation, washing and neutralization of calcium hydroxide and during the input of dispersing agent.

The separation and recovery of PCC according to the invention may be coupled with any known process to prepare PCC, which is based on causticizing or carbonizing reactions.

However, the invention is preferably coupled with a process in which fine calcium carbonate of homogeneous grain size is prepared by causticizing, the grain size being essentially 0.2 - 0.4  $\mu\text{m}$ . Separation and recovery of such a substance has been found quite advantageous. The method for preparation comprises three steps, in which

- in the first step calcium hydroxide dispersion is mixed with a sodium carbonate solution,
- in the second step the reaction is allowed to continue without essentially stirring the reaction mixture, until the desired grain size is achieved, and
- in the third step the reaction is quenched.



For the first reaction step particles of calcium hydroxide are formed to be of as equal size as possible and preferably only about 50 times larger at the most than the grain size of the calcium carbonate particles to be prepared. To the reaction with carbonate ions, hydrated calcium oxide is introduced in which at least 80 % of the particles are smaller in grain size than 3  $\mu\text{m}$ . It is especially preferred to bring lime hydrate and soda into contact, during which the crystal nuclei are formed, in a fast rotating mixer which produces large turbulent mixing and cutting forces. For example, the shock mixer described above is suitable for this purpose.

In the second step of the method, the reaction between calcium hydroxide and the carbonate ions is allowed to take place essentially without mixing the reaction mixture until the desired particle size of calcium carbonate is reached.

The reaction is quenched in the third stage of the method after a preselected period of time by subjecting the reaction mixture to strong mixing forces. The length of the period of time is determined according to the size and shape of particles desired. Most suitably quenching is performed with a powerful mixer using strong turbulence, shocks and cutting. Also for this purpose, it is preferred to use a shock mixer.

The following example describes a preferred embodiment of the invention, in which an excess of carbon dioxide in comparison to the amount of the hydroxy compounds is dissolved into the washing solution, and released inside the filter cake in order to dry this.

### Example

Filtration is commenced by pumping the suspension to be filtered into the filter. At the beginning some particles to be filtered may be transferred to the filtrate, and the filtrate is recycled back to the input when needed, should this occur. When the filter cake has begun to form, filtration is continued until the cake is sufficiently thick and the filtration rate is significantly reduced. The pressure is then, for example, 6 bar. Thereafter, washing water is pumped to the filter, to which carbon dioxide gas has been dissolved, for example, at a pressure of 5 bar, and the washing water is pumped at greater than 5 bar pressure to the

filter. When a sufficient replacement in washing has been achieved, the input valve is closed and the filtration is continued such that the pressure is continuously reduced. This causes carbon dioxide to be released from the water (in this case) in the chamber of the filter, which causes the liquid to be forced lower and through the filtered cake. Further reduction  
5 of pressure causes further release of carbon dioxide gas, which finally forces almost all the free water from the filtered cake, and simultaneously dries the cake by finally forcing the carbon dioxide gas through the cake. Carbon dioxide gas neutralizes residual alkalinity in the filtered cake by reacting with the hydroxy compounds at the same time.

- the pressure in the filtrate zone is reduced gradually, in order to cause the gas to bubble and to prevent the filtered cake from shrinking and cracking.

16. The method according to any of the preceding Claims 12 - 15, wherein the filtered cake is heated when the pressure in the filtrate zone is reduced.

17. The method according to the preceding Claim 16, wherein water vapor (steam) is led to the filtering zone.

18. An apparatus for recovering calcium carbonate from a hydroxy compound-containing reaction mixture, the apparatus comprising

- at least one pressure filtration unit (3 - 5; 21), with which calcium carbonate can be separated from the reaction mixture, and
- a tank for the wash liquid (8 - 10; 35) connected to the pressure filtering unit, from which washing liquid may be added to the filtration unit for washing calcium carbonate,

characterized in that

- the washing liquid tank (35) is equipped with an input line for carbon dioxide, through which carbon dioxide can be added to the washing liquid.

19. The apparatus according to Claim 18, which comprises

- at least two separate pressure filtration units (21), each with its own input line through which the liquid to be filtered, wash liquid for calcium carbonate and the neutralizing solution for calcium carbonate may be added to the filtration unit.

20. The apparatus according to Claim 19, wherein each of the pressure filtration units (21) may be used independently of the other units.

21. The apparatus according to Claim 19 or 20, wherein the pressure filtration units comprise stacks of filtering disks (21) and that the input line is arranged in the center of the end of the stack of filtration disks, which effects a short transfer distance for liquid and homogeneous filling and wash.

22. The apparatus according to Claim 19, 20 or 21, wherein there are 4 - 10 stacks of filtering disks (21).

5 23. The apparatus according to any of the preceding Claims 19 - 22, comprising a combined unit for transferring disks and tightening (23) the stacks, with which a new stack of filtering disks can be arranged in the place of a stack removed from operation (24).

10 24. The apparatus according to any of the preceding Claims 19 - 23, which comprises a balance for weighing pressure filtration units (24) removed from operation in order to check the intactness of filtering fabrics or similar filtering means.

25. The apparatus according to any of the preceding Claims 19 - 23, wherein the top part of the stack of filtering disks comprises a compressible rubber disk, which has been fitted to buffer the pressure of the filtration unit between the various process steps.

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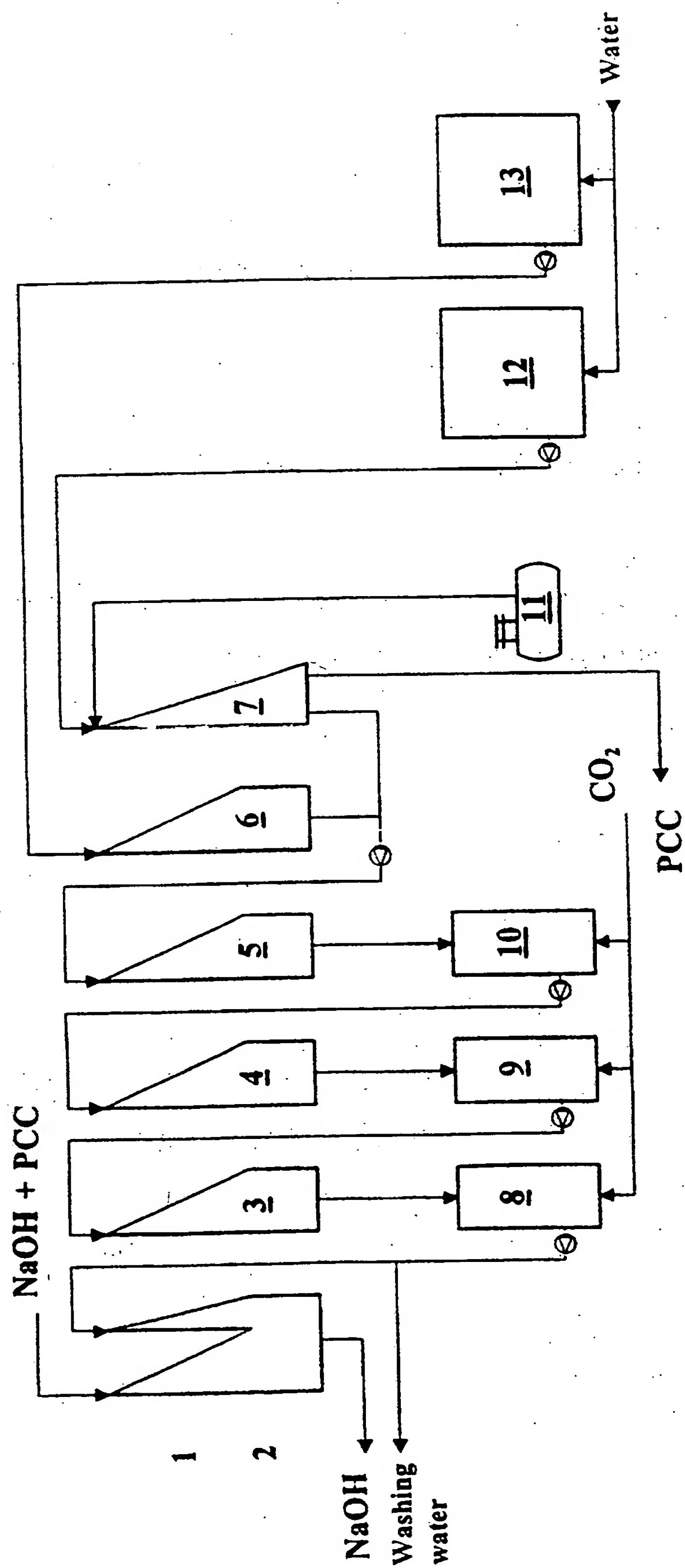
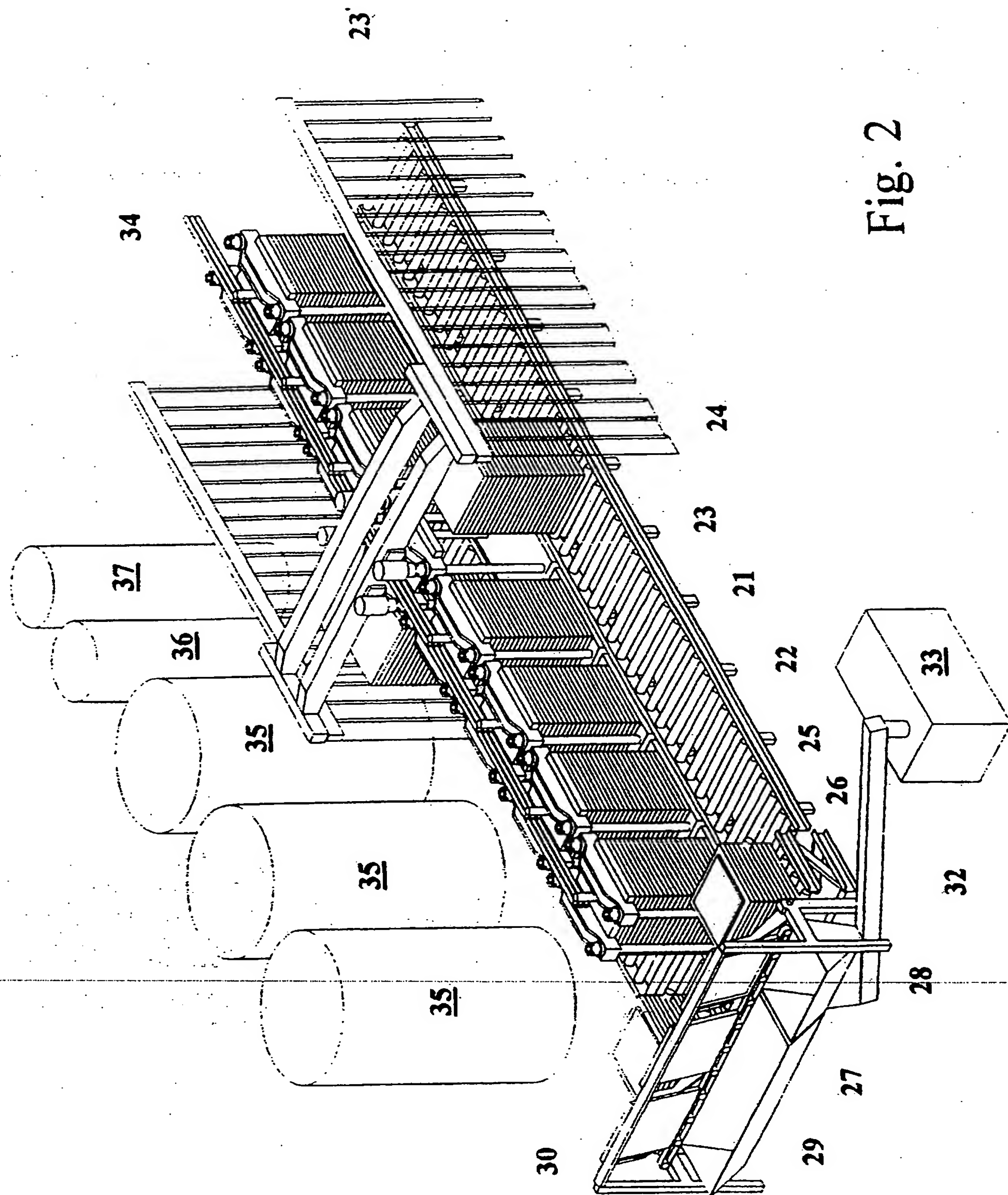


Fig. 1





1  
INTERNATIONAL SEARCH REPORT

International application No.

PCT/FI 97/00238

## A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C01F 11/18

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	FI 950411 B (KAUTAR OY), 31 July 1996 (31.07.96), abstract	1
X	DE 3110896 A1 (FOSTER WHEELER ENERGY CORP.), 30 Sept 1982 (30.09.82), page 4, line 1 - page 5, line 20; page 11, line 3 - line 14, abstract	1-4

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

## \* Special categories of cited documents:

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Date of the actual completion of the international search

4 July 1997

Date of mailing of the international search report

28 -07- 1997

Name and mailing address of the ISA/  
Swedish Patent Office  
Box 5055, S-102 42 STOCKHOLM  
Facsimile No. +46 8 666 02 86

Authorized officer

Johan von Döbeln  
Telephone No. +46 8 782 25 00

**INTERNATIONAL SEARCH REPORT**  
Information on patent family members

03/06/97

International application No.

PCT/FI 97/00238

Patent document cited in search report			Publication date	Patent family member(s)		Publication date
FI	950411	B	31/07/96	AU	4541696 A	21/08/96
				WO	9623728 A	08/08/96
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DE	3110896	A1	30/09/82	NONE		
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